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HEATS OF SOLUTION IN LIQUID AMMONIA

Dorsey C. Thomas Jr.

June 1947
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By

Approved By

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HEATS OF SOLUTION IN LIQUID AMMONIA

Introduction

By a comparison of the properties of liquid ammonia and water, one can see a great similarity between the two solvents. At the same time there exists some very striking differences. The work that is being done to-day originates from the work of Franklin and his co-workers. The work on the heats of solutions was studied at Brown University by Kraus and Ridderhof, Kraus and Prescott, and Kraus and Schmidt. The more recent source of information concerning the heats of solutions have come from Dr. F.C. Schmidt and his co-workers at the Butterfield Laboratories at Union College.

The present work consists of measurements of the heats of solution of guanidine hydrochloride in this solvent. Also there will be presented a detailed description of the method of operation of the calorimeter which is being used.
Apparatus

Plate (1) shows a detailed diagram of the calorimeter and the delivery system. This apparatus is essentially an adiabatic calorimeter. The ammonia is drawn into a special tank which is connected directly to the calorimeter and the ammonia is drawn off as needed.

The calorimeter is made of Monex glass. The radiation constant is 0.10 cals./deg./min. and the calorimeter constant is 9.16 cals./deg.

In the operation of the calorimeter system, all valves except (A), (B), and (I) are opened. The system is evacuated by means of a vacuum pump which is operated by a 1/2 horsepower motor. The system is evacuated to less than 10 microns and then closed off by closing valves (B), (C), (D), (E), and (G). Also by closing these valves the system is now ready for the delivery of ammonia from the special tank and the pipette is separated from the rest of the system.

The pipette is enclosed by a Dewar flask containing boiling ammonia at -33 deg. C. Valve (A) is opened and the anhydrous ammonia from the special tank is condensed in the pipette against a pressure head of approximately 200 mm. of Hg. When the desired amount of the anhydrous ammonia has been collected, valve (A) is closed.

In order to pass the ammonia into the calorimeter, the calorimeter is enclosed in the same manner as the pipette and allowed to come to a temperature of -33 deg. C. by the boiling ammonia in the jacket. Valve (C) is opened and the ammonia is distilled from the pipette and allowed to condense in the calorimeter at approximately 900 mm. of Hg. The time interval for this operation is approximately 1 1/2 to 2 hours. Extreme care must be observed at this stage so
that none of the ammonia will be boiled out of the system at the pressure head. Slow boiling will prevent this. However, it has been found that after about 1/2 of the total amount has been distilled over, the ammonia can be forced over by using slightly warmed alcohol as a heater. However, it is recommended that this is not done until 1/2 of the total amount of ammonia has gone over.

When the ammonia has been introduced into the calorimeter, valve (C) is closed, and the system is allowed to come to equilibrium. This can be determined by means of a copper-constantine thermocouple and potentiometer. When the potentiometer reading has become constant for a period of 2-3 minutes, equilibrium has been reached. Generally, if a waiting period of 15 minutes is allowed, the system is at equilibrium.

Previous to this, the weighed sample has been placed in a fragile glass bulb and connected to the outside by means of a rod passing through a gas tight seal.

Prior to making the run, the collector flask is filled with distilled water. Valve (C) is opened, drawing off any uncondensed ammonia in the system. The volume is 105 ml. Valve (C) is then closed.

In making the run, two heat values are obtained. First, the major heat effect, measured by the amount of ammonia vaporized and collected in the collector flask, and the second, the minor heat effect, measured by the change in temperature of the system and determined by the thermocouple.

Just prior to starting the stirrer, all valves except (H) are closed. This permits the ammonia evolved to flow only to the
collector flask. The stirrer, operated by a solenoid and mechanically operated circuit breaker, is started. The temperature is recorded and any change in the temperature is noted. The temperature should be constant before the bulb is broken.

When this value is constant, the sample bulb is broken and the salt is permitted to go into solution. As has been stated, the major heat effect is measured by the amount of vaporized ammonia collected in the collector flask. The minor heat effect is measured by the rise or lowering of the temperature as shown by the potentiometer. The potentiometer is balanced every 15 seconds and the readings are recorded. These are converted to temperature by previous calibration data.

The ammonia in the aqueous solution is titrated with standard sulfuric acid, and the heat, proportional to the amount of ammonia present, is calculated.

The total heat of solution is the sum of the major and minor heats. From the total heat for the sample, the molar heat of solution is calculated. Also calculated is the moles of ammonia per mole of salt.
Experimental

The ammonia used was obtained from the Mathieson Alkali Company, and found to contain 1/2 to 1 1/2% water. In order to remove the water and obtain anhydrous ammonia, the ammonia was drawn into the special tank which contained sodium and allowed to dry.

The heat of vaporization of the ammonia was 327.7 cal./deg. (7) The specific heat at -35 deg. was 1.067 cal./deg. The amount of ammonia used was 49.46 grams.

The salt, guanidine hydrochloride, was prepared by R. A. Vingee of the American Cyanamid Corporation, at Stamford Conn. The purity was checked by a chloride analysis and was found to be 37.37% and the calculated value was 37.15%. The salt was assumed to be pure.

An approximate value of the solubility was determined by adding weighed amounts of the salt to 50 ml. of anhydrous liquid ammonia. It was found that 2.39 grams of the salt dissolved.

To determine the amount of ammonia evolved during the reaction, the aqueous solution of ammonia was titrated with standardized \( \text{H}_2\text{SO}_4 \). The acid was standardized against sodium carbonate, Methyl Red being used as the indicator. The normality of the acid was found to be 0.1128.

The samples were prepared by placing the salt in a fragile glass bulb and the bulb was evacuated to about 10 microns. This removed any excess water. The bulb was then sealed off while under vacuum.

The runs were made as stated in the previous section. The table of results are given. As can be seen the results of the runs
were erratic and checks could not be obtained. It was not possible to obtain a satisfactory curve. The results are shown in table (1).

These results led to a second analysis. This time 20 grams of the salt were dissolved in 200 ml. of anhydrous ammonia. The solution was allowed to stand until the ammonia had evaporated off. (A drying tube was inserted in the top of the Dewar flask and filled with NaOH to prevent any water from coming in contact with the salt.)

A chloride analysis was carried out and the percent chloride was found to be (1) 33.53% and (2) 35.71%. Calculation showed that if \( \text{NH}_2\text{Cl} \) had formed or if there had been solvation by ammonia then the value should be 31.618%. It was, therefore, concluded that this salt apparently solvates, but ammonia is lost at room temperature, and the analysis shows partial solvation. Since guanidine is so strong a base, it is probable that no transfer of proton had occurred, then there would be no variation in the percentages in the various samples. It must be noted that no attempt was made to make the samples homogeneous.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Moles of Salt</th>
<th>Molar Heat</th>
<th>Moles of H\textsubscript{2}O per Mole of Salt</th>
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Summary

An attempt was made to determine the molar heats of solution over a wide range of concentrations for the salt guanidine hydrochloride. As has been stated, no checks could be obtained and no curve could be obtained. An attempt was made to explain these differences by the partial solvation of the salt by the ammonia.

Also a detailed description of the operation of the calorimeter has been given with the physical constants which apply.

Acknowledgment

I wish to thank Dr. F.C. Schmidt for his patient and guiding influence in this problem. I should also like to thank him for his help in solving another problem which has been bothering me.

[Signature]

Dorsey C. Thomas Jr.
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